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Diffusion and dissolution in a reactive porous medium: Mathematical modelling and numerical simulations

P. Moszkowicz[a], J. Pousin[b,*], F. Sanchez[a]

[a]*Laboratoire de Chimie Physique Appliquée et Environnement, National Institute of Applied Sciences in Lyon, 20 av. Einstein, F-69621 Villeurbanne Cedex, France*

[b]*Mathematical Modelling and Scientific Computing Laboratory, CNRS URA 740, National Institut of Applied Sciences in Lyon, 20 av. Einstein, F-69621 Villeurbanne Cedex, France*

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Abstract

In this work a simple mathematical model for diffusion and dissolution in reactive porous medium is presented. The case of lime and lead in solid phase enclosed in cement matrices is considered more specifically. A numerical method based on finite difference and on a marching technique is proposed and some numerical results are provided. In a simple case, the results obtained are compared with numerical results available in literature.

Keywords: Reaction–diffusion; Phase change; Jumping nonlinearities; Semilinear parabolic–hyperbolic

AMS classification: 35B40; 35M10; 65C20; 65M20; 80A32

0. Introduction

This work originates from an attempt to model from mathematical and numerical points of view, the leaching of ions from cement matrices used for waste solidification and waste storage. Notice that in such a context the reaction zones are nonlocalized. Here, we present a simple model for leaching of several ionic chemical species accounting for phase change (dissolution of solid species), diffusion and chemical reactions. Then, we consider more specifically the case of lime and lead leaching (i.e. lime and lead exist in solid phase). We propose a numerical method based on a marching technique to approximate numerically the mathematical model for diffusion and dissolution introduced previously. Finally some numerical results are discussed, and in the case of one chemical species, we compare our method with results available in literature.

* Corresponding author. E-mail: pousin@insa.insa-lyon.fr.

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The outline of this article is as follows: In Section 1 under reasonable physical assumptions, we derive the simple mathematical model we propose for diffusion and dissolution of a multi species mixture in a porous reactive medium. In Section 2, by using finite difference and a marching technique, we introduce the approximated problem for the case of lime and lead. Some numerical results we obtained are presented, and in the case of one chemical species in solid phase (lime) these results are compared with existing results.

1. Mathematical model for diffusion and dissolution

In this article we do not consider the process of diffusion and dissolution on the microscopic scale of a single pore of the cement matrix, but on the macroscopic scale appropriate for measurement of phenomena described. Interstitial solution of cement is assumed to be diluted. Due to the small size of pores of hydrated cements, thermal convection can be neglected and the pressure gradient is low (see [1] for a partial justification). Thus interstitial solution is supposed to be at rest, therefore transport of ions into interstitial solution results only from a diffusion process.

For $1 \leqslant k \leqslant L$, we denote by C_k the molar concentration of ionic chemical species k in liquid phase, supplied by dissolution, and for $L+1 \leqslant k \leqslant N$ the others species in liquid phase.

Assume that a ionic species k produced by dissolution comes only from one species in solid phase. Then for $1 \leqslant p \leqslant M$ we denote by S_p the molar concentration of chemical species p in solid phase. For $1 \leqslant k \leqslant N$, we denote by $R_k(C_1, \ldots, C_N)$ the molar rate of production of species k due to chemical reactions in liquid phase, and for $1 \leqslant k \leqslant L$ we denote by $F_k(C_1, \ldots, C_N, S_p)$ the molar production rate of species k yielding from dissolution of species p in solid phase. We set $l(p)$ the following set of indexes:

$$l(p) = \{k \in \{1, \ldots, L\} \text{ s.t. species } p \text{ in solid phase gives off species } k\}.$$

Let $\theta, 0 < \theta < 1$ be the porosity of the medium assumed to be constant. Denote by Ω the cylindrical domain filled with hydrated cement:

$$\Omega = \{(x, y, z) \in \mathbb{R}^3,\ x^2 + y^2 < 1,\ 0 < z < 1\}. \tag{1.1}$$

Now we state the equations resulting from conservation principle. The relative number of moles of species k filling an arbitrary subdomain V of Ω is given by

$$\int_V \theta C_k \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z, \quad 1 \leqslant k \leqslant N. \tag{1.2}$$

According to Fick's law, the outgoing diffusive flux of ionic species k, q_k through the surface ∂V (the boundary of subdomain V) expresses as

$$q_k = D_k \nabla C_k \cdot \boldsymbol{n}, \quad 1 \leqslant k \leqslant N, \tag{1.3}$$

where the constant D_k stands for the diffusive coefficient and $\boldsymbol{n}$ for the outgoing normal to the volume V. The change in the number of moles of species k in an arbitrary smooth subdomain V of

Ω at time t should equal the flux through the boundary of V, ∂V plus the number of moles produced by chemical reactions in liquid phase plus the number of moles of species k that dissolution yields. We have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \theta C_k \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = \int_{\partial V} \theta D_k \nabla C_k \cdot \boldsymbol{n}\,\mathrm{d}\sigma$$

$$+ \int_V \theta R_k(C_1, \ldots, C_N)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z + \int_V (1-\theta)F_k(C_1, \ldots, C_N, S_p)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z, \quad 1 \leqslant k \leqslant N. \tag{1.4}$$

By using Green's formula, and since Eqs. (1.4) are valid in every smooth subdomain V, we have

$$\theta\partial_t C_k - \operatorname{div}(\theta D_k \nabla C_k) = \theta R_k(C_1, \ldots, C_N) + (1-\theta)F_k(C_1, \ldots, C_N, S_p), \quad 1 \leqslant k \leqslant N. \tag{1.5}$$

It remains to specify the dissolution kinetic equations which, because of mass balance between solid and liquid phases read:

$$\partial_t S_p = -\sum_{k \in l(p)} F_k(C_1, \ldots, C_N, S_p), \quad 1 \leqslant p \leqslant M. \tag{1.6}$$

Now, let us give the major assumptions of the model we propose. Chemical reactions in liquid phase are at equilibrium, thus $R_k \equiv 0$ for $1 \leqslant k \leqslant N$; the solution in liquid phase is diluted; electrical equilibrium is reached, and the functions representing the physical quantities depend only on z variable as space variable. We still denote by the same symbol these functions. For $0 < T$ be given, Eqs. (1.5) and (1.6) become

$$\theta\partial_t C_k - \operatorname{div}(\theta D_k \nabla C_k) = (1-\theta)F_k(C_1, \ldots, C_N, S_p), \quad 1 \leqslant k \leqslant N \quad \text{in } (0,1)\times(0,T), \tag{1.7}$$

$$\partial_t S_p = -\sum_{k \in l(p)} F_k(C_1, \ldots, C_N, S_p), \quad 1 \leqslant p \leqslant M \quad \text{in } (0,1)\times(0,T). \tag{1.8}$$

We denote by sgn^+ the following real function:

$$\operatorname{sgn}^+(z) = \begin{cases} 1 & \text{if } 0 < z, \\ 0 & \text{otherwise.} \end{cases} \tag{1.9}$$

If $0 < \alpha$ is a given constant, then possible expressions for functions F_k are:

$$\begin{aligned} &F_k \equiv 0 \quad \text{for } L+1 \leqslant k \leqslant N, \\ &F_k(C_1, \ldots, C_N, S_p) = \alpha \operatorname{sgn}^+(S_p)[C_k^* - C_k], \quad 1 \leqslant k \leqslant L, \end{aligned} \tag{1.10}$$

where C_k^* stands for thermodynamical equilibrium concentrations of ionic species k.

In what follows, we describe, for the solution, thermodynamical equilibrium relationships for the concentrations, for the chemical reactions and electrical equilibrium relationships. We denote by lower cases the chemical species and by upper cases their concentration. Since we deal with a solution we have to consider species constituting water: OH^- and H_3O^+. We denote by C_{N+1}, C_{N+2} the concentration of ions OH^- and H_3O^+. For $1 \leqslant k \leqslant L$, $L+1 \leqslant q \leqslant N$,

$1 \leqslant p \leqslant M$ we denote by K_p^k, K_q the positive equilibrium constants and by A_q^k, A_k the nonnegative stoechiometric coefficients.

Dissolution relationships read:

$$s_p \rightleftharpoons A_p^k c_k + A_p c_{N+1}, \quad K_p^k = C_k^{A_p^k} C_{N+1}^{A_p} \text{ if } 0 < S_p,\ 1 \leqslant k \leqslant L,\ 1 \leqslant p \leqslant M. \tag{1.11}$$

Chemical reactions read:

$$c_q \rightleftharpoons A_q^k c_k + A_q c_{N+1}, \quad K_q = \frac{C_k^{A_q^k} C_{N+1}^{A_q}}{C_q},\ 1 \leqslant k \leqslant L,\ L+1 \leqslant q \leqslant N, \tag{1.12}$$

$$c_{N+1} + c_{N+2} \rightleftharpoons 2H_2O, \quad 10^{-14} = C_{N+1} C_{N+2}. \tag{1.13}$$

Suppose that c_k for $1 \leqslant k \leqslant L$ and c_q for $L+1 \leqslant q \leqslant I$ are positive ions and that c_q for $I+1 \leqslant q \leqslant N$ are negative ions. If v_l denotes the valence of species c_l for $1 \leqslant l \leqslant N$, then the electrical equilibrium relationship reads:

$$C_{N+2} + \sum_{k=1}^{L} v_k C_k + \sum_{q=L+1}^{I} v_q \frac{C_k^{A_q^k} C_{N+1}^{A_q}}{K_q} = C_{N+1} + \sum_{q=I+1}^{N} v_q \frac{C_k^{A_q^k} C_{N+1}^{A_q}}{K_q}. \tag{1.14}$$

Notice that the Eqs. (1.11) to (1.14) allow to compute the equilibrium concentrations C_k^* for $1 \leqslant k \leqslant L$. If s_p a species in solid phase yielding a species c_k in liquid phase vanishes then the corresponding equation in (1.11) is no longer valid. So to compute the equilibrium concentrations C_l^*, $l \neq k$, we use in Eq. (1.14) the values of the function C_k solution to Eqs. (1.7), (1.8).

Now in order to simplify the presentation let us consider the case of calcium and lead leaching from a cement matrix neglecting the species $CaOH^+$ and $PbOH^+$ in liquid phase. If $[\cdot]$ denotes the molar concentration, then we set:

$$C_1 = [Ca^{2+}],\ C_2 = [Pb^{2+}],\ C_3 = [Pb(OH)_3^-],\ C_4 = [OH^-],\ C_5 = [H_3O^+],$$

$$S_1 = [Ca(OH)_2],\ S_2 = [Pb(OH)_2].$$

The thermodynamical, the chemical and the electrical equilibriums read:

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-, \quad K_1^1 = C_1 C_4^2 \text{ if } 0 < S_1,$$

$$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-, \quad K_2^2 = C_2 C_4^2 \text{ if } 0 < S_2,$$

$$Pb(OH)_3^- \rightleftharpoons Pb^{2+} + 3OH^-, \quad K_3 = \frac{C_2 (C_4)^3}{C_3}, \tag{1.15}$$

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O, \quad 10^{-14} = C_3 C_4,$$

$$C_5 + 2C_1 + 2C_2 = C_3 + C_4.$$

Note that a linear combination of second and third relationships in (1.15) yields a dissolution relationship for species $Pb(OH)_3^-$ which will be accounted in what follows. Now let us introduce some notations in order to state the mathematical problem which modelizes the diffusion and

dissolution of chemical species. If $\mathrm{diag}(a_1, \ldots, a_3)$ denotes the diagonal matrix the entries of which are $a_1, \ldots, a_3$ and if C^* denotes the equilibrium concentrations of chemical species c, we set

$$\beta = \frac{1-\theta}{\theta}, \quad \mathbb{D} = \mathrm{diag}(D_1, D_2, D_3), \quad F(C, C^*, S) = \mathrm{sgn}^+(S)[C^* - C],$$

$$\begin{aligned} &\boldsymbol{C} = (C_1, C_2, C_3)^{\mathrm{T}}, \quad \boldsymbol{C}^* = (C_1^*, C_2^*, C_3^*)^{\mathrm{T}}, \quad \boldsymbol{S} = (S_1, S_2)^{\mathrm{T}}, \\ &\boldsymbol{F}(\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}) = (F(C_1, C_1^*, S_1),\ F(C_2, C_2^*, S_2),\ F(C_3, C_3^*, S_2))^{\mathrm{T}}, \\ &\boldsymbol{G}(\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}) = (F(C_1, C_1^*, S_1),\ F(C_2, C_2^*, S_2) + F(C_3, C_3^*, S_2))^{\mathrm{T}}, \end{aligned} \tag{1.16}$$

where T denotes the transposition, $l(1) = \{1\}$; $l(2) = \{2, 3\}$. We will say that V is a nonnegative, negative, respectively, nonpositive, positive real vector if all its components are nonnegative, negative, respectively, nonpositive, positive. Finally for $0 < T$ given we define Q_T by

$$Q_T = \{(z, t) \in \mathbb{R}^2, z \in (0, 2),\ t \in (0, T)\}. \tag{1.17}$$

Then the mathematical model derived previously is called Problem (P) and reads:

For $0 < \alpha$, $\boldsymbol{C}^0, \boldsymbol{S}^0$ defined in $(0, 2)$, given, find nonnegative real valued vector functions $\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}$ and real functions C_4^*, C_5^* defined in Q_T and satisfying:

$$\partial_t \boldsymbol{C} - \mathbb{D}\partial_x^2 \boldsymbol{C} = \beta \boldsymbol{F}(\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}) \text{ in } Q_T, \tag{1.18}$$

$$\partial_t \boldsymbol{S} = -\alpha \boldsymbol{G}(\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}) \text{ in } Q_T, \tag{1.19}$$

$$\partial_z \boldsymbol{C}(0, t) = 0;\ \boldsymbol{C}(2, t) = 0 \text{ in } (0, T), \tag{1.20}$$

$$\boldsymbol{C}(z, 0) = \boldsymbol{C}^0(z) \text{ in } (0, 2), \tag{1.21}$$

$$\boldsymbol{S}(z, 0) = \boldsymbol{S}^0(z) \text{ in } (0, 2), \tag{1.22}$$

$$K_1^1 = C_1^*(C_4^*)^2 \text{ if } 0 < S_1, \quad K_2^2 = C_2^*(C_4^*)^2 \text{ if } 0 < S_2, \tag{1.23}$$

$$K_3 = \frac{C_2^*(C_4^*)^3}{C_3^*}, \quad 10^{-14} = C_4^* C_5^*, \tag{1.24}$$

$$C_5^* + 2C_1^* + 2C_2^* = C_3^* + C_4^*. \tag{1.25}$$

If for $1 \leqslant p \leqslant 2$ S_p vanishes then in Eqs. (1.24)–(1.25), C_p^* is replaced by C_p solution to equation (1.18). Notice that until the vector $\boldsymbol{S}$ is positive, then the equilibrium concentrations $\boldsymbol{C}^*$; C_4^*, C_5^* are constant in Q_T, and the equations (1.23)–(1.26) are not coupled with the other equations. In that case, the mathematical Problem (P) reduces to Problem (1.18)–(1.22):

For $0 < \alpha$, $\boldsymbol{C}^0$, $\boldsymbol{S}^0$, $\boldsymbol{C}^*$ given, find nonnegative real valued vector functions $\boldsymbol{C}$, $\boldsymbol{S}$ defined in Q_T and satisfying Eqs. (1.18)–(1.22)

Remarks 1.1. The conditions (1.20) are boundary conditions and espress that the bottom of the sample is isolated and that the top sample concentration is known.

The relation (1.25) is an equation for C_4^*.

Problem (1.18)–(1.25) is a free boundary problem due to the unknown interfaces between solid and liquid phases. In that model, if vector function $\boldsymbol{S}$ is continuous, the interfaces can be recovered a posteriori as points $\{(z,t) \in Q_T$ such that $S_p(z,t) = 0$ for $1 \leqslant p \leqslant 2\}$. From a numerical point of view, the proposed model avoids to follow interfaces, which is crucial in the case of several species in solid phase. Further, such a model allows to handle diffusive coefficients D_k which are different for each species k.

Let us mention that in the case of one species (we consider only the lime leaching Ca^{2+}) existence and uniqueness of solutions to Problem (P) have been established (see [3]). This result of existence and uniqueness applies to Problem (1.18)–(1.22). If a component of vector $\boldsymbol{S}$ vanishes, then the question of existence and uniqueness is more involved.

Let us end the derivation of mathematical model with the following result.

Lemma 1.2. *Assume $X^0 \in L^2(0,2)$, $0 \leqslant X^0$, $l \in L^2(Q_T)$, $0 \leqslant l$ and α a positive constant to be given. Then the function X defined by*

$$X(z,t) = \left(X^0(z) - \alpha \int_0^t l(z,s)\,\mathrm{d}s \right)^+ \quad \forall (z,t) \in Q_T$$

is the unique solution in distributional sense to the following equation:

$$\partial_t X = -\alpha \operatorname{sgn}^+(X) l \quad \text{in } Q_T,$$

$$X(z,0) = X^0(z) \quad \text{in } (0,2).$$

Proof. For the proof see for example [3, Theorem 2.1, p. 8]. □

2. Approximated problem and numerical results

Problem (1.18)–(1.22) is a semilinear parabolic–hyperbolic problem. Thus finite difference and a marching techniques are introduced to approximate numerically this problem.

By using Lemma 1.2 Problem (1.18)–(1.25) can be rewritten as:

For $0 < \alpha$, $\boldsymbol{C}^0, \boldsymbol{S}^0$ given, find nonnegative real valued vector functions $\boldsymbol{C}$, $\boldsymbol{C}^*$, $\boldsymbol{S}$ and real functions C_4^*, C_5^* defined in Q_T and satisfying

$$\partial_t \boldsymbol{C} - \mathbb{D}\partial_z^2 \boldsymbol{C} = \beta \boldsymbol{F}(\boldsymbol{C}, \boldsymbol{C}^*, \boldsymbol{S}) \text{ in } Q_T, \tag{2.1}$$

$$S_q(z,t) = \left(S_q^0(z) - \alpha \sum_{k \in l(q)} \int_0^t C_k^*(z,s) - C_k(z,s)\,\mathrm{d}s \right)^+ (z,t) \in Q_T,\ 1 \leqslant q \leqslant 2, \tag{2.2}$$

$$\partial_z \boldsymbol{C}(0,t) = 0,\ \boldsymbol{C}(2,t) = 0 \quad \text{in } (0,T), \tag{2.3}$$

$$\boldsymbol{C}(z,0) = \boldsymbol{C}^0(z) \text{ in } (0,2), \tag{2.4}$$

$$K_1^1 = C_1^*(C_4^*)^2 \text{ if } 0 < S_1, \quad K_2^2 = C_2^*(C_4^*)^2 \text{ if } 0 < S_2, \tag{2.5}$$

$$K_3 = \frac{C_2^*(C_4^*)^3}{C_3^*}, \quad 10^{-14} = C_4^* C_5^*, \tag{2.6}$$

$$C_5^* + 2C_1^* + 2C_2^* = C_3^* + C_4^*. \tag{2.7}$$

If for $1 \leqslant p \leqslant 2$, S_p is null then, in Eqs. (2.6)–(2.7), C_p^* is replaced by C_p solution to Eq. (2.1).

Now we introduce some notations useful for stating the approximated problem. Let $0 < M$, $0 < N$ be given, we set $h = 2/M$, $\tau = T/N$, and we define the points (z_i, t_n) by

$$z_i = ih, \quad t_n = n\tau, \qquad 0 \leqslant i \leqslant M,\ 0 \leqslant n \leqslant N.$$

We denote by

$$\begin{aligned} &\boldsymbol{C}_i^n = (C_{1_i}^n, C_{2_i}^n, C_{3_i}^n)^{\mathrm{T}}, \quad \boldsymbol{S}_i^n = (S_{1_i}^n, S_{2_i}^n)^{\mathrm{T}}, \\ &\boldsymbol{C}_i^{*^n} = (C_{1_i}^{*^n}, C_{2_i}^{*^n}, C_{3_i}^{*^n})^{\mathrm{T}}, \quad C_{4_i}^{*^n}, \quad C_{5_i}^{*^n}, \\ &\boldsymbol{F}_i^n(\boldsymbol{C}^n, \boldsymbol{C}^{*^n}, \boldsymbol{S}^n) = (F(C_{1_i}^n, C_{1_i}^{*^n}, S_{1_i}^n), F(C_{2_i}^n, C_{2_i}^{*^n}, S_{2_i}^n), F(C_{3_i}^n, C_{3_i}^{*^n}, S_{2_i}^n))^{\mathrm{T}} \end{aligned} \tag{2.8}$$

approximations of vectors $\boldsymbol{C}, \boldsymbol{S}, \boldsymbol{C}^*, \boldsymbol{F}$ and of C_4^*, C_5^* at points (z_i, t_n) for $0 \leqslant i \leqslant M$, $0 \leqslant n \leqslant N$.

Then Problem (1.18)–(1.25) is approximated by the following problem: assume the families $\{\boldsymbol{C}_i^n\}_{i=0}^M$, $\{\boldsymbol{C}_i^{*^n}\}_{i=0}^M$, $\{\boldsymbol{S}_i^n\}_{i=0}^M$ and $\{C_{4_i}^{*^n}, C_{5_i}^{*^n}\}_{i=0}^M$ are known, then find $\{\boldsymbol{C}_i^{n+1}\}_{i=0}^M$, $\{\boldsymbol{C}_i^{*^{n+1}}\}_{i=0}^M$, $\{\boldsymbol{S}_i^{n+1}\}_{i=0}^M$ and $\{C_{4_i}^{*^{n+1}}, C_{5_i}^{*^{n+1}}\}_{i=0}^M$ satisfying

$$\boldsymbol{C}_0^{n+1} = \boldsymbol{C}_1^{n+1}, \tag{2.9}$$

$$\frac{\boldsymbol{C}_i^{n+1} - \boldsymbol{C}_i^n}{\tau} - \frac{1}{h^2}\mathbb{D}[\boldsymbol{C}_{i-1}^{n+1} - 2\boldsymbol{C}_i^{n+1} + \boldsymbol{C}_{i+1}^{n+1}] = \beta \boldsymbol{F}_i^{n+1}, \quad 1 \leqslant i \leqslant M-1, \tag{2.10}$$

$$\boldsymbol{C}_M^{n+1} = 0, \tag{2.11}$$

$$S_{p_i}^{n+1} = \left(S_{p_i}^0 - \alpha \sum_{k \in I(p)} \sum_{r=0}^{n+1} \tau(C_{k_i}^{*^r} - C_{k_i}^r)\right)^+ = \left(S_{p_i}^n - \alpha\tau \sum_{k \in I(p)} (C_{k_i}^{*^{n+1}} - C_{k_i}^{n+1})\right)^+, \quad 1 \leqslant p \leqslant 2, \tag{2.12}$$

$$\boldsymbol{C}_i^0 = \boldsymbol{C}^0(z_i), \tag{2.13}$$

$$K_1^1 = C_{1_i}^{*^{n+1}}(C_{4_i}^{*^{n+1}})^2 \text{ if } \exists j \text{ s.t. } 0 < S_{1_j}^{n+1}, \quad K_2^2 = C_{2_i}^{*^{n+1}}(C_{4_i}^{*^{n+1}})^2 \text{ if } \exists j \text{ s.t. } 0 < S_{2_j}^{n+1}, \tag{2.14}$$

$$K_3 = \frac{C_{2_i}^{*^{n+1}}(C_{4_i}^{*^{n+1}})^3}{C_{3_i}^{*^{n+1}}}, \quad 10^{-14} = C_{4_i}^{*^{n+1}} C_{5_i}^{*^{n+1}}, \tag{2.15}$$

$$C_{5_i}^{*^{n+1}} + 2C_{1_i}^{*^{n+1}} + 2C_{2_i}^{*^{n+1}} = C_{3_i}^{*^{n+1}} + C_{4_i}^{*^{n+1}}, \quad 0 \leqslant i \leqslant M. \tag{2.16}$$

If for $1 \leqslant p \leqslant 2$, S_p^{n+1} is null then $C_{p_i}^{*n+1}$ is replaced by $C_{p_i}^{n+1}$ solution to equations (2.10). Whereas until the vectors S_p^{n+1} are not null, the equilibrium concentrations are constants (i.e. do not depend on indices i and n).

Eqs. (2.9)–(2.16) are nonlinear. Let us indicate which algorithm is used to solve these equations in the case where the equilibrium concentrations are constant. First the equilibrium concentrations C_l^*, for $1 \leqslant l \leqslant 5$ are computed by solving the Eqs. (2.14)–(2.16) with a Newton procedure. For the sake of clearness we describe the Picard fixed point algorithm only for computing $\{C_{1_i}^{n+1}\}_{i=0}^{M}$ since the same algorithm is used for $\{C_{2_i}^{n+1}\}_{i=0}^{M}$, $\{C_{3_i}^{n+1}\}_{i=0}^{M}$. We denote by $\mathbb{A}$ the tridiagonal $M \times M$ matrix defined by

$$\mathbb{A}_{i,j} = \begin{cases} -1 & \text{if } j = i-1, \\ 2 & \text{if } j = i, \\ -1 & \text{if } j = i+1 \end{cases} \quad \text{for } 1 \leqslant i \leqslant M, \quad \mathbb{A}_{1,1} = 1, \ \mathbb{A}_{1,2} = -1,$$

and $\mathbb{I}_V$ stands for the diagonal matrix $\operatorname{diag}(V_0, \ldots, V_{M-1})$. For $0 \leqslant q$ the $\mathbb{R}^M$ vectors $\boldsymbol{C}_1^q$, $\boldsymbol{C}$, $\mathbf{sgn}^q$ are respectively defined by: $(C_{1_0}^q, \ldots, C_{1_{M-1}}^q)^{\mathrm{T}}$, $(C_0, \ldots, C_{M-1})^{\mathrm{T}}$, $(\operatorname{sgn}^+(S_{1_0}^q), \ldots, \operatorname{sgn}^+(S_{1_{M-1}}^q))^{\mathrm{T}}$, where $S_{1_i}^q = [S_{1_i}^n - \alpha\tau(C_1^* - C_{1_i}^q)]^+$ are given by formula (2.12). Then for a given small $\varepsilon > 0$, the fixed point algorithm reads:

$\boldsymbol{C}^0 = \boldsymbol{C}_1^n, \boldsymbol{S}_1^0 = \boldsymbol{S}_1^n$ for $0 \leqslant q$ assume $\boldsymbol{C}^q, \boldsymbol{S}_1^q$ are known, compute $\mathbf{sgn}^q$ and compute $\boldsymbol{C}$ satisfying

$$\left[\mathbb{I} + \frac{\tau}{h^2}\mathbb{A} + \tau\mathbb{I}_{\mathbf{sgn}^q}\right]\boldsymbol{C} = \tau\mathbb{I}_{\mathbf{sgn}^q}\boldsymbol{C}_1^* + \mathbb{I}\boldsymbol{C}^n,$$

$$S_{1_i}^{q+1} = [S_{1_i}^n - \alpha\tau(C_1^* - C_{1_i})]^+, \tag{2.17}$$

if $S_{1_i}^{q+1} = 0$, compute C_1^* by solving (2.14)–(2.16)

If $\varepsilon \leqslant \|\boldsymbol{C}^q - \boldsymbol{C}\|$, $q = q+1$ and solve (2.17)
else $\boldsymbol{C}_1^{n+1} = \boldsymbol{C}$, $S_{1_i}^{n+1} = S_{1_i}^q$, $0 \leqslant i \leqslant M$.

If the equilibrium concentrations are no more constant we have to add the equations (2.14)–(2.16) and to compute the equilibrium concentrations for each step (2.17). Notice that in such a situation the equations for $\boldsymbol{C}_{k_i}^{n+1}$, $1 \leqslant k \leqslant 3$, $0 \leqslant i \leqslant M-1$ are coupled and are simultaneously computed in a procedure similar to (2.17). Now let us end this section with some numerical results.

2.1. *The case of lime leaching; comparison with other methods*

For that test case only one chemical species in solid and liquid phases are taken into account ($Ca(OH)_2$, Ca^{2+}). Moreover, if the initial concentration in liquid phase equals equilibrium concentration and if the initial concentration in solid phase is constant, then the medium can be considered as semi-infinite. So the problem of lime leaching looks like a 1-D Stefan's problem for which an analytical solution is known (see, e.g., [2]). Due to the null flux condition at $z = 0$, the Stefan's problem solution is not a solution to lime leaching problem, but it can be proved that it is a good approximation of the solution to lime leaching problem. In Fig. 1 concentration of Ca^{2+} is plotted as a function of time at $z = 1.2$ and for $D_1 = 1.3 \cdot 10^{-11}$; $S_1^0(z) = 0.1$, $\forall z \in (0,2)$. The

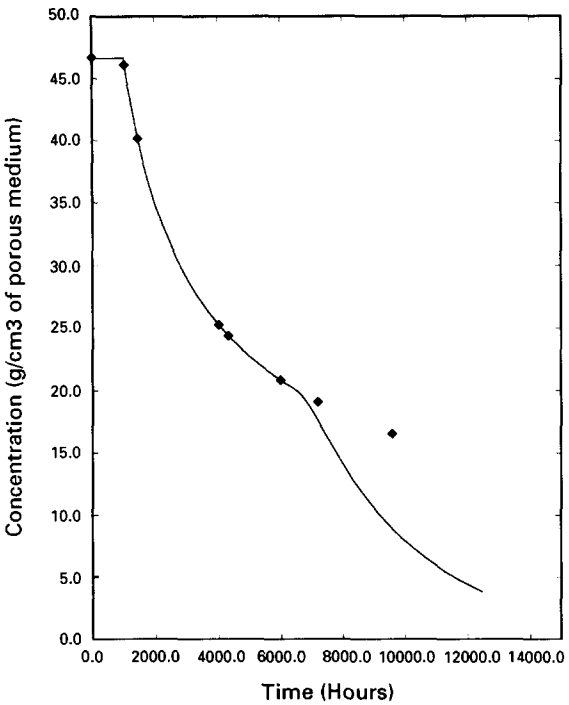

Fig. 1.

concentration of Ca^{2+} is computed with the Stefan's problem solution (line with diamonds), with a moving interface strategy as in [1] (solid line) and with the present method (dashed line). The results between Stefan's problem solution and the two other methods diverge when the concentration of species in solid phase vanishes in a neighbourhood of the point under consideration because the hypothesis of semi-infinite medium becomes false. Fig. 2 represents on a logarithmic scale the flux of species Ca^{2+} at $z = 2$ as a function of time. The flux is a straight line until the concentration of $Ca(OH)_2$ in solid phase vanishes in a neighbourhood of this point. The slope of this line equals 0.5. Fig. 4 represents the flux of species Ca^{2+} at $z = 2$ as a function of time when the initial concentration of species Ca^{2+} in liquid phase is no longer equal to the equilibrium concentration but is given by Fig. 3.

2.2. *The case of lime and lead leaching*

For that case we take equilibrium concentration profiles for the species in liquid phase as the initial profiles. For the species in solid phase, we take a uniform initial profile for $Ca(OH)_2$, $S_1^0(z) = 0.1$ and the following profile for $Pb(OH)_2$:

$$S_2^0(z) = \begin{cases} 0.1 & \text{if } 0 \leqslant z \leqslant 1, \\ 0 & \text{if } 1 < z < 1.7, \\ 0.1 & \text{if } 1.7 \leqslant z \leqslant 2. \end{cases}$$

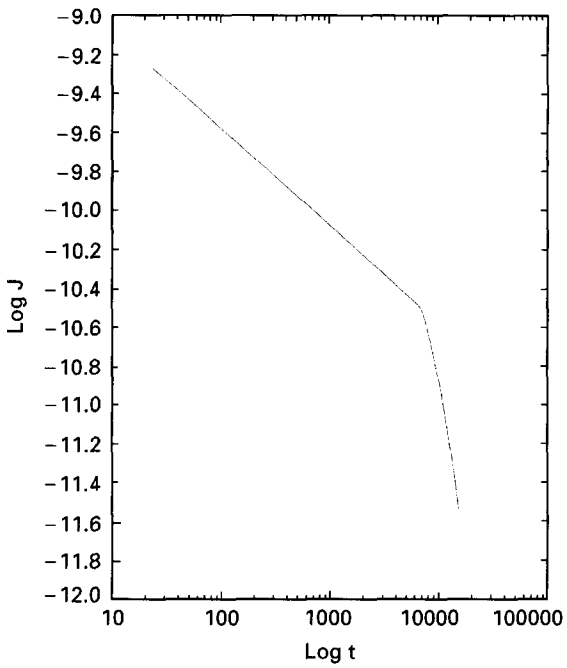
-9.0
-9.2
-9.4
-9.6
-9.8
-10.0
-10.2
-10.4
-10.6
-10.8
-11.0
-11.2
-11.4
-11.6
-11.8
-12.0
Log J
10
100
1000
10000
100000
Log t

Fig. 2.

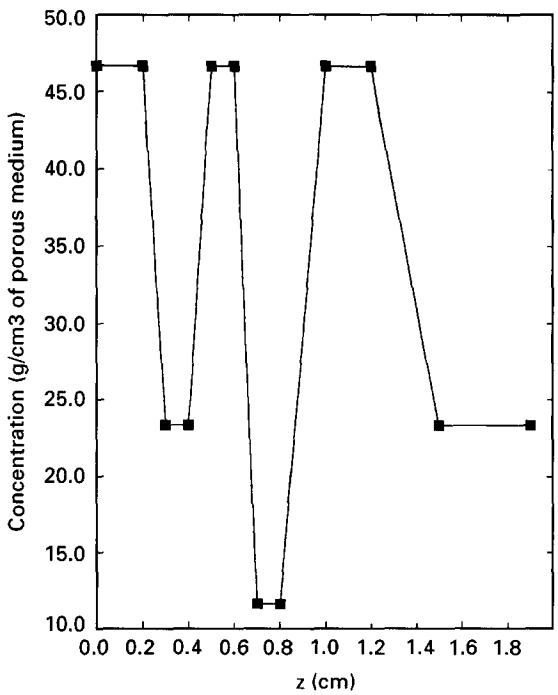
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
Concentration (g/cm3 of porous medium)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8
z (cm)

Fig. 3.

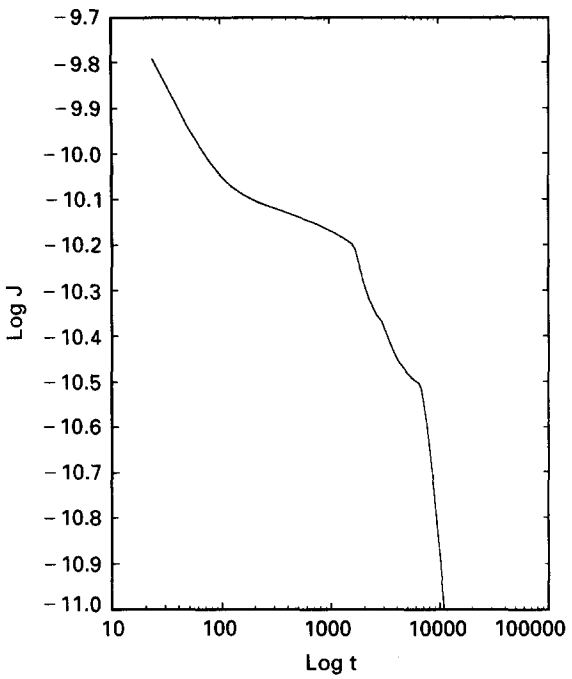
-9.7
-9.8
-9.9
-10.0
-10.1
-10.2
-10.3
-10.4
-10.5
-10.6
-10.7
-10.8
-10.9
-11.0
Log J
10
100
1000
10000
100000
Log t

Fig. 4.

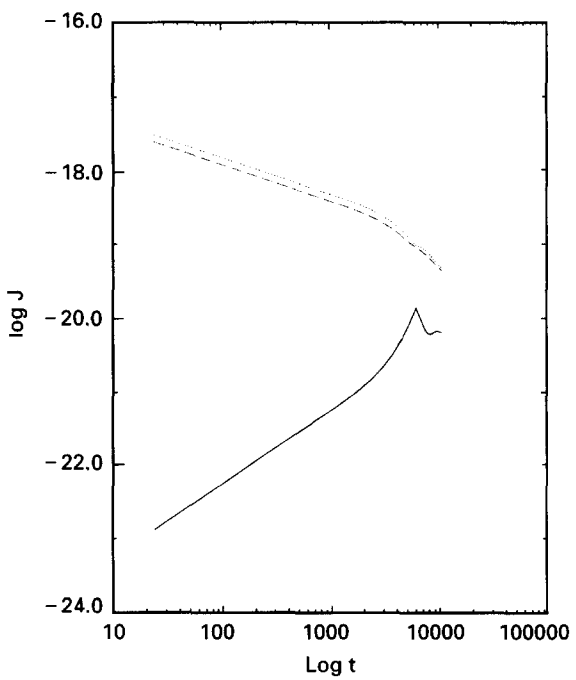
-16.0
-18.0
-20.0
-22.0
-24.0
log J
10
100
1000
10000
100000
Log t

Fig. 5.

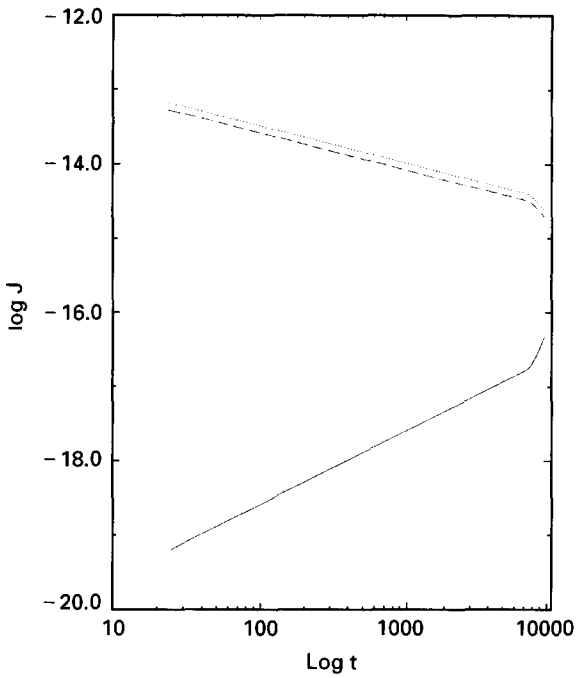

Fig. 6.

The diffusive coefficients for chemical species are all equal to $1.3 \cdot 10^{-11}$. In Fig. 5 is reported the flux of lead Pb^{2+} plus $Pb(OH)_3^-$ (dashed line), the flux of Pb^{2+} (continued line) and the flux of $Pb(OH)_3^-$ (dotted line) as functions of time at $z = 2$. Similarly as in the case where only lime was taken into account, the flux of species Ca^{2+} is a straight line the slope of which is 0.4977. The flux of lead is also a straight line the slope of which is 0.4965. This phenomena is a consequence of the existence of lime and lead in solid phase during the simulation time, therefore the diffusion and dissolution processes for the lime and for the lead are not coupled. Moreover, the dissolution of lead does not occur due to a too large pH number.

Now we consider the case where there is no lime in solid phase ($S_1^0(z) = 0$), the initial profile for lead in solid phase is uniform and is equal to 10^{-9}, and we take uniform equilibrium profiles in liquid phase. The diffusive coefficients are given by: (for lime) $D_1 = 1.3 \cdot 10^{-11}$, (for lead) $D_2 = D_3 = 10^{-15}$. In Fig. 6 the fluxes of lead Pb^{2+} plus $Pb(OH)_3^-$ (dashed line), of Pb^{2+} (solid line) and of $Pb(OH)_3^-$ (dotted line) are reported as functions of time.

3. Conclusion

The presented mathematical model allows to handle complex situations, many chemical species can be modelized which was not possible with a moving interfaces strategy. Moreover, the numerical method presented is robust and yields good results.

References

[1] M. Buil, E. Revertegat and J. Olivier, A model of attack of pure water or undersaturated lime solutons on cement, in: T.M. Gilliam and C.C. Wiles, Eds., *Stabilization and Solidification of Hazardous Radioactive, and Mixed Wastes*, 2nd Vol., STP 1123 (American Society for Testing and Materials, Philadelphia, 1992) 227–241.
[2] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1983).
[3] P. Moszkowicz, J. Pousin and F. Sanchez, Diffusion and dissolution in a reactive porous medium: mathematical modelling, Preprint No. 164, Equipe d'Analyse Numérique Lyon Saint Etienne URA CNRS 740, 1994.